3D Hierarchical nano-flake/micro-flower Iron fluoride with hydration water induced tunnels for secondary lithium battery cathodes

Ying Bai ^{a, ‡, *}, Xingzhen Zhou ^{a, ‡}, Chun Zhan ^{b, ‡}, Lu Ma ^c, Yifei Yuan ^{b, d}, Chuan Wu ^{a, e}, Mizi Chen ^a, Guanghai Chen ^a, Qiao Ni ^a, Feng Wu ^{a, e}, Reza Shahbazian-Yassar ^d, Tianpin Wu ^f, Jun Lu ^{b, *} and Khalil Amine ^{b, *}

^a Beijing Key Laboratory of Environmental Science and Engineering, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

^b Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South, Cass Avenue, Lemont, IL 60439, USA

^c Department of Chemistry and Biochemistry, Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, USA; and X-ray Science Division, Argonne National Laboratory 9700 South Cass Avenue, Argonne, Illinois 60439, USA

^d Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, 845 West Taylor Street, Chicago, IL 60607, USA

^e Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing 100081, P.R. China

^f X-ray Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

[‡] These authors contribute equally to this work.

*E-mail: membrane@bit.edu.cn (Y. Bai), junlu@anl.gov (J. Lu) and amine@anl.gov (K.A.)

Abstract: As a potential multi-electron electrode material for next generation lithium ion batteries, iron fluoride (FeF_3) and its analogues are attracting much more attentions. Their microstructures are the key to achieve good electrochemical performances. In this work, $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ nano-flakes precursor with high crystallinity and flower-like morphology is synthesized successfully, by a liquid precipitation method using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NH_4HF_2 as raw materials. The formation and the crystal growth mechanisms of the $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursors are investigated and discussed. After different temperature heat-treatment and followed by ball-milling with Super P, the as-prepared $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ and FeF_3/C nanocomposites are used as cathode materials for lithium ion batteries. The $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite exhibits a noticeable initial specific capacity of 187.1 mAh g^{-1} and reversible specific capacity of 172.3 mAh g^{-1} at 0.1C within a potential range of $2.0\text{-}4.5\text{V}$. The capacity retention is as high as 97.33% after 50 cycles. Combined with HRTEM test, it confirms that the hydration water is not harmful but useful, namely, the tunnel phase formed with the hydration water is crucial to unobstructed Li^+ diffusion, and therefore leading to excellent electrochemical performances.

Keywords: lithium ion batteries, cathode materials, iron fluoride, liquid precipitation, hydration water

1. Introduction

Over the last two decades, lithium ion battery (LIB) has been playing a more and more important role in energy supplying for portable electronic products and energy storage, for its advantages in efficiency, environmental benignity, cost and safety.[1-5] In spite of the several breakthroughs in the chemical of cathode materials, the theoretical gravimetric capacities of commercial cathode materials are still insufficient for practical applications such as the electric vehicles and grid-level energy storage.[6-8] In order for higher capacity of the LIB cathode, various new forms of energy storage materials are investigated, and the

multi-electron materials have drawn more and more attention due to their high theoretical specific capacities.[9] Among them, iron fluoride is very attractive because of its high specific capacity (237 mAh g^{-1} per electron transfer), high operating voltage, non-toxicity and low-cost.[10,11]

FeF_3 was reported as the cathode materials for lithium ion batteries as early as 1997. It showed a high-voltage charge-discharge behavior but delivered a reversible capacity of only 80 mAhg^{-1} in a discharge voltage region from 2V to 4.5V at a low rate, which was far below the theoretical capacity.[12] In fact, the actual capacity of FeF_3 is reduced largely by its poor electronic and ionic conductivity.[13-15] In order to improve the electrochemical performance of FeF_3 , many methods have been introduced, such as FeF_3 /carbon composite prepared by high energy milling with conductive agents[13-17], nanofabrication[18-22], thin films obtained by Pulsed Laser Deposition technique[23-25], in site coating[26-27], metal doping[28-29] and so on. Among all of them, high energy milling with conductive agents is a simple and effective method as the grain size can be significantly reduced with the conductive network established at the same time.[30] As a result, the Li^+ diffusion pathways within particles are shortened and the electronic transportation is facilitated significantly.

Iron fluorides exist with different chemical compositions, either with or without hydration water, for instance, FeF_3 , $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$, etc. It is generally accepted that moisture should be restrictly avoided in lithium ion batteries, because water is highly reactive towards carbonate-based electrolyte as well as metallic lithium, and the as-generated by-products will degrade the electrode materials. However, it is interesting that most of these hydrous iron fluorides have electrochemical activities. Therefore, it is of great importance to understand what is the role of hydration water, and why hydration water will not act like the moisture.

In previous works, there are various methods to synthesize the iron-based fluoride materials, for instance, liquid-precipitate method[28,31-34], evaporation method[35], sol-gel

method[36] and solvothermal method[28,30,37-38]. Toxic HF is the most commonly used fluoride source in these methods, which may lead to some safety issues.[18,31-33,35-37,39-40] Besides, some ionic-liquids was also applied as fluoride source but its high cost should be a concern for industry application.[19,21,38,41] In fact, solution chemistry is a good approach, because it can build an suitable environment full of water, which can be easily introduced into the lattice of the as-prepared iron fluoride. Therefore, a liquid-precipitate method is applied in the present study, where NH_4HF_2 is selected as fluoride source, because it is less volatilizable and safer than HF. Moreover, the gaseous product of NH_4HF_2 is expected to form porous structures for the as-prepared particles. $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor with flower-like morphology is prepared through this approach. Active $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposites were obtained after calcination at different temperatures and the subsequent ball-milling with Super P. The impact of composition and crystal structure on the electrochemical performance of the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ nanocomposite are discussed.

2. Experimental Section

2.1. Sample synthesis

All chemical reagents were of analytical grade and used as received without any further purification. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and NH_4HF_2 were selected as raw materials and the polyethylene glycol (PEG 20000) was used as a dispersant. The preparation process is showed in Scheme 1. Firstly, PEG (15g) was dissolved in a co-solvent of ethanol (150ml) and deionized water (20ml) in duplicate. One was added to $\text{Fe}(\text{NO}_3)_3$ ethanol solution (160 ml, $0.25\text{mol} \cdot \text{L}^{-1}$); the other was transferred to a Teflon ware, and then a required amount of NH_4HF_2 powder was dissolved in it. With peristaltic pump, the $\text{Fe}(\text{NO}_3)_3$ solution was added drop-wise to NH_4HF_2 solution accompanying by stirring. After 12 hours' standing time, pale yellow precipitates were obtained. Washed by deionized water and ethanol alternately for

three times, the precipitates were vacuum-dried at 80°C for 12h and cooled down naturally. In order to control its hydration water content, the as-prepared precursor was then calcined at various temperatures from 200 to 500°C, and the obtained samples were named as S200, S300, S400, S500, respectively. The calcined iron fluoride samples and synthesis conditions are listed in Table S1. To further improve the conductivity of the calcined iron fluoride sample, a conductive agent, namely Super P, was added (iron fluoride: SP = 85:15 by weight). After high energy ball-milling at 300 rpm for 3h, the mixture was converted into an iron fluoride/carbon nanocomposite, as shown in Scheme 1 and Table S1. The final products were named as S200/SP, S300/SP, S400/SP, S500/SP, respectively.

2.2. Structural characterization

To understand the thermal stability of the precursor, and select suitable calcine temperature, TG-DTA was conducted with a Seiko 6300 instrument at a heating rate of 10°C min⁻¹ from room temperature to 700°C under argon atmosphere. The crystal structures of the as-synthesized materials were collected on a Rigaku 2400 XRD with Cu K α radiation ($\lambda=0.15418\text{nm}$) between 10° and 80° 2 θ at a scan rate of 8° 2 θ min⁻¹. The morphologies were investigated by using a FEI Quanta 250 FESEM. The HRTEM was done using a JEOL 3010 equipped with a 300 KV LaB6 electron source. The atomic modeling was established using Crystal Maker software.

2.3. Electrochemical evaluation

The nanocomposites were mixed with Super P and a polyvinylidene fluoride (PVDF) binder at a weight ratio of 8:1:1 in N-methy-1-2-pyrrolidinone (NMP) solvent. The as-obtained slurry was then coated on an aluminum foil and vacuum-dried at 120°C for 12h. The laminate was punched into disks with a diameter of 11mm as cathode electrodes and the areal density is about 1.0 mg/cm². Lithium foil was used as the counter electrode and reference electrode; the electrolyte was 1M solution of LiPF₆ dissolved in a mixed solvent of ethylene

carbonate (EC), dimethyl carbonate (DMC) and ethylene methyl carbonate (EMC) (1:1:1 by volume). The coin cells were assembled in an argon-filled glove box, using a porous polypropylene Celgard 2400 as separator. All cells were aged for 12h before testing.

Charge/discharge tests were performed with a CT2001A instrument to evaluate the electrochemical capacities. The CV experiments and EIS were conducted with a CHI604D electrochemical workstation. CV tests were measured at a scanning rate of 0.1 mVs^{-1} between 2.0 and 4.5V. The frequency range was from 10^6 Hz to 10^{-1} Hz at potentiostatic signal amplitudes of 5 mV.

The X-ray Absorption Spectroscopy (XAS) measurements for the Fe K-edge (7112 eV) were completed in transmission mode on the bending-magnet beamline of the Advanced Photon Source (9-BM-C) in Argonne National Laboratory. The incident beam was monochromatized by using a Si (111) fixed-exit, double-crystal monochromator. In situ XAS experiments were made on the coin cells with a window of 5mm diameter sealed with 50- μm -thick Kapton tape. The cells were cycled with a MACCOR cycler. XANES data reduction followed standard methods using the ATHENA software package.

3. Results and Discussion

3.1 Crystal structure and morphology

Figure 1 shows morphology and X-ray diffraction (XRD) pattern of the precursor. Scanning electron microscope (SEM) images revealed that the precursor nano-flakes have thicknesses about 50-100 nm and the flakes form beautiful flower-like shapes (Figure 1a-b). It can be clearly seen that the diffraction peaks of precursor match well with $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (tetragonal structure, $P4/n$ space group, JCPDS 32-0464), without impurity peaks observed (Figure 1c).

To understand the self-assembly process of the $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor, the apparent morphologies of the particles at different aging time were recorded, as shown in Figure 2. The

growing process is visualized by Figure 2 a-f, and the corresponding mechanism is illustrated by Figure 2 g.

The slow assembling process seems to be a two-step procedure, namely, self-template and self-aggregation. At the end of stirring, the morphology of the precipitate is irregular. After standing for 3h, most of the particles grew a plate shape by themselves and partial self-aggregations have taken place, just as shown in Figure 2 b. The polyethylene glycol (PEG) plays an important role in this step. By adding PEG to the mixture solvent, the viscosity became higher and the fluidity turned lower, which affected the reaction kinetics. As a result, the reactive interface could be increased and the reaction time will be reduced[42], which both sides benefit the growth and formation of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ crystals. The seeds take a thermodynamically unfavorable plate-like shape, which is a typical case of kinetic-controlled growth.[43] With increasing standing time, the nearby plate crystals adjust themselves to close each other and form interpenetration twin spontaneously and orderly, as shown in Figure 2 c and d. This step is driven by the oriented attachment mechanism.[44] The longer the standing time is, the better the morphology will be. After 12h, the well-developed flower-like particles are obtained. In addition, with increasing standing time, the edges of the particles become thinner, which are in favor of a well-knit structure. Little difference between Figure 2 e and f was observed, which indicating that the 12h standing time is just enough.

According to the result of the thermogravimetric - differential thermal analysis (TG-DTA), the weight loss of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ happened in four steps (Figure S1), including the removal of absorbed water and the phase transformations of crystals, which are explained by reactions (1)-(3). Therefore, the as-prepared precursor was pre-sintered at 120°C in vacuum oven to remove the absorbed water and then transferred into tube furnace to be calcinated. 200°C, 300°C, 400°C and 500°C were chosen as the target temperatures and the whole calcining process was in pure argon to avoid the unexpected reaction with oxygen. To distinguish the products well, the calcinated powders were marked as S200, S300, S400 and S500

corresponding to the calcination processes 200°C (3h), 200°C (3h) - 300°C (3h), 200°C (3h) - 400°C (3h) and 200°C (3h) - 500°C (3h), respectively. After being ball milled with Super P (SP), they were reconverted to S200/SP, S300/SP, S400/SP and S500/SP respectively. All the sample names and corresponding synthesis conditions are listed in Table S1.

The main component of the as-prepared iron fluoride sample changes with increasing calcination temperature, which is indicated by XRD results (Figure S2). The main phase of S200 is $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, demonstrating reaction (1) has taken place under 200°C, which is in accordance with the TG-DTA results (Figure S1). PEG evaporates during the temperature region from 200°C to 300°C, which is reflected by SEM (Figure S3). When the temperature is lower than 250°C (the boiling point of PEG), most PEG still remain in material, supporting the original morphology (Figure S3a). However, the particle shape easily changes when the PEG evaporates at 300°C (Figure S3b). It is no doubt that S300 is purer than S200. As expected, when the calcination temperature reaches at 400°C, the crystal phase has changed totally and the main content is converted to FeF_3 , which can be described by reaction (2). The production of FeF_2 also means that reaction (3) is taking place. The main component of S500 remains FeF_3 , but much Fe_2O_3 is detected as well as little FeF_2 . Besides, the material is pulverizing gradually and S500 turns to nanoscale fine particles (Figure S3c-d). Reaction (3) is responsible for this phenomenon.

Theoretically, with increasing temperature and further decomposition of FeF_3 , the content of FeF_2 should increase as well. However, large amount of Fe_2O_3 are detected, so it is speculated that the as-produced FeF_2 reacts with O_2 in air after calcination to become Fe_2O_3 due to its poor thermodynamic stability, which can be summarized as reaction (4). What's more, when the particle size has been decreased to nanoscale (Figure S3d), the large specific

surface area results in more active sites, and thus promotes the reaction between O₂ and FeF₂. As a result, it is Fe₂O₃ rather than FeF₂ that is detected obviously in S500.

The different phases are further verified by the high resolution transmission electron microscopy (HRTEM) results. Figure 3 illustrates the atomic scale imaging of the particles after being treat at 300 °C (a, b) and 500°C (c). The particle in Figure 3a exhibits a tunneled FeF₃·0.33H₂O phase (Cmcm) being viewed along [310] zone axis, as confirmed by the [310] atomic model of the theoretical tunneled FeF₃·0.33H₂O phase in the inset. The solid yellow balls represent Fe1 (0,0.5, 0) and the circular yellow balls stand for Fe2 (0.25, 0.25, 0). Fe2 columns are invisible due to their limited number along [310] direction and the resulted weak scattering contribution to form the final contrast, while Fe1 are visible because they have a dense pack along [310] direction that leads to the final contrast. Overall, the tunnel structure is obvious and can surely facilitate the transportation of Li⁺. At the same time, we also found FeF₃ phase (R-3h) in S300 sample (Figure 3b), which indicated that reaction (2) took place as well. But the concentration of FeF₃ is no doubt very low because it cannot be detected by XRD (Figure S2). Figure 3c is for the particle after 500 °C treatment, where only the FeF₃ phase with R-3h space group is observed. Therefore, treatment at higher temperature is able to improve the phase transition from the tunneled phase FeF₃·0.33H₂O to the new phase FeF₃, while further electrochemical experiments are required to compare the performance of these two phases.

In order to improve conductivity of the material, the powders after calcination were ball milled with Super P to get the nano-composites, as showed in Scheme 1. The SEM images (Figure S4) show that the particle sizes of the nano composites are around 100-200nm which is smaller than particles sizes (0.1-1.7μm) after ball milling the rectangular micro-bar and the hollow prism/cylinder at higher ratote speed (320 rpm). [30, 37] It follows that such 3D micro-flower iron fluoride, self-assembled by about 50-100nm thick nano-flakes, is more

easily ground into nanoparticles through the processes of micro-flower converting into nano-flakes, subsequent into nanoparticles.

3.2 Electrochemical performance

The electrochemical properties of different iron fluoride samples are studied in coin cells employing lithium foil as counter/reference electrode and S200/SP, S300/SP, S400/SP, S500/SP as the working electrodes. The specific capacities are calculated based on the quality of iron fluorides only. S200/SP, S300/SP, S400/SP and S500/SP deliver initial discharge specific capacities of 163.4, 187.1, 198.1 and 170 mAh g⁻¹, respectively (Figure 4a). Because of the irreversible formation of solid electrolyte interphase (SEI) in the first cycle, the specific capacities in the first cycle are not stable.[6,29-30,45-47] The specific capacities in the second cycle are consequently regarded as reversible. Both S300/SP and S400/SP deliver the high reversible capacities. However, with the increase of cycle number, the specific capacity of S400/SP fades fast. As shown in Figure 4b, the capacity retentions are calculated based on reversible capacities. Four samples seem to be divided into two groups: S200/SP and S300/SP constitute the FeF₃·0.33H₂O group (based on the constituent) and the FeF₃ group is composed of S400/SP and S500/SP. The capacity retentions of the former group are obviously higher than those of the other group. Herein, the cycling performance of FeF₃·0.33H₂O is superior to that of FeF₃, which is very similar to previous report.[37]

To test the rate performances of different samples, the cells are discharge-charged at various current densities from 0.1C to 1C and finally back to 0.1C (Figure 4c). S300/SP shows superior rate performances. It exhibits a high initial discharge capacity of 193 mAh g⁻¹, and achieves reversible capacities of 173, 161, 150, and 146 mAh g⁻¹ at 0.1C, 0.2C, 0.5C and 1.0C, respectively. The discharge capacity of S300/SP at 1C in the voltage range of 2.0-4.5V is higher than that of FeF₃·0.33H₂O/C [30, 37] and FeF₃·0.33H₂O/CMK-3 [48] (about 130 mAh g⁻¹). Superior rate capability of S300/SP can be ascribed to smaller nanocomposites via ball milling nano-flake/micro-flower precursor with SP. Because smaller nanoparticle

contributes to shorting the path of electronic and ionic transmission path, resulting in improving the reaction kinetics of Li^+ . [13, 49] In addition, after an activation process for S300/SP during high-rate cycles, it can achieve a high reversible capacity of 181 mAh g^{-1} when the discharge rate recovers to 0.1C .

Electrochemical impedance spectroscopy (EIS) analysis was conducted to explore the electrochemical behaviors of different iron fluoride samples (Figure 4d). The EIS plot consist of one semicircle in the high frequency region and a sloping line in the low frequency region. The semicircle reflects the charge transfer resistance (R_{ct}), and the sloping line is related to the diffusion impedance (Z_w) of Li^+ in the solid matrix. Figure S5 demonstrates the corresponding equivalent circuit model in which R_{Ω} represents the impedance of electrolyte. The values of R_{ct} are listed in Table S2. It is shown that R_{ct} of S300/SP is much lower than those of S200/SP, S400/SP and S500/SP, which is in line with the results of capacity retention in Figure 4b.

In order to determine the oxidation state evolution of the Fe element in the S300/SP electrode, Fe K-edge X-ray absorption near edge structure (XANES) spectra were collected continuously while the cell was under cycling. Fe K-edge XANES were also recorded from FeO and Fe_2O_3 standards as references for Fe(II) and Fe(III). Figure 5a and b compared the normalized Fe K-edge XANES spectra during the first discharge and charge. The Fe K-edge of the S300/SP in the beginning is at about 7126 eV which is close to the Fe K-edge of Fe_2O_3 , showing the oxidation state of Fe is +3 in the uncycled electrode. During the discharge, the Fe K-edge shifted to a lower energy due to the reduction of the Fe(III). At the end of discharge, the Fe K-edge is still higher than Fe(II) in FeO, showing an average oxidization state higher than +2. This result indicates that the Fe(III) was not fully reduced to Fe(II) when discharge to 2V. In the following charge to 4.5V, the Fe K-edge shifted gradually back to the about 7126 eV, corresponding to the oxidation of Fe to Fe(III). According to the above result, the discharge process of S300/SP can be declared by reaction (5), which also explains why the specific capacity of S300/SP is less than the theoretical.

To better illustrate the XANES spectra evolution, 2D contour plots of Fe k-edge XANES spectra recorded during the first two cycles of the cell and the corresponding voltage profile are presented in Figure 5c and d. The evolution of the XANES spectra, especially the back and forth shift of the edge, is well correlated with discharge-charge process. In the second cycle, the evolution was repeated in a symmetrical pattern corresponding to the symmetrical voltage profile, indicating high reversibility of the electrochemical lithiation/delithiation reactions of the S300/SP during the discharge and charge process. It is corresponding to the good cycle performance of shown in Figure 4b.

So far, S300/SP shows the best electrochemical properties, but the reasons behind the differences among different samples need discussing. Actually, different electrochemistry properties for the iron fluoride samples are ascribed to the different compositions of these materials, as displayed in Figure S2. The active constituent of S200 and S300 is $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ while S400 and S500 have already converted to FeF_3 . Apparently, the traces of hydration water play an important role in the structure and subsequently impact the electrochemical performance.

The structures of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ and FeF_3 can help illustrating the impact of hydration water, as shown in Figure 6. (002) plane of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ is corresponding to the strongest diffraction peaks of S200 and S300 while (012) plane of FeF_3 is corresponding to the strongest diffraction peaks of S400 and S500 (Figure S2). In the structures of both $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ and FeF_3 , iron atom is surrounded by six fluorine atoms in a form of octahedron. [37,50] The adjacent octahedrons connect with each other, sharing the apices of fluorine atoms. But the connection ways are totally different in $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ or FeF_3 . For $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, six octahedrons are connected via corner-sharing, forming lots of special and huge hexagonal cavities in $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ (Figure 6a). The water molecules are located in the center of cavities to stabilize the structure. The growing of (002) plane forms large inner

tunnel structure in $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ (Figure 6c), which can facilitate the insertion and extraction for Li^+ . As a result, Li^+ can be more easily intercalated and extracted during the charge-discharge process in $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, which results in the excellent cycle and rate performances compared with other samples (Figure 4b-c). Besides, the existence of hydration water could reduce the ionicity and improve the electronic conductivity significantly[37], which is beneficial to the lower R_{ct} values of S300/SP. Compared with S300/SP, S200/SP shows the inferior specific capacity in spite of the same iron fluoride. It is because that amorphous PEG cannot evaporate at 200 °C and has negative effects on the capacity as an impurity residue.

As for FeF_3 , it shows a distorted ReO_3 structure without the hydration water (Figure 6b and d). The octahedrons are closer with each other to form narrow tunnel, making Li^+ accommodating more difficult. This distinguishes FeF_3 from $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ in terms of capacity and cycle performance, as shown in Figure 4. The cyclic voltammetry (CV) results (Figure S6) and discharge-charge curves (Figure S7) also demonstrate the differences between $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ and FeF_3 . The CV curves of S200/SP and S300/SP are similar, with only one couple of reversible redox peaks detected, which are related to the lithium ion insertion and extraction process, as declared by reaction (5). However, for S400/SP and S500/SP samples, two pairs of redox peaks are detected obviously after the first scan loop. Both the discharge-charge curves of S200/SP and S300/SP present a discharging platform at ~2.7V and a charging platform at ~3.2V. However, the discharge-charge curves of S400/SP and S500/SP both present two discharging platforms at ~3.3V and ~3.0V, and corresponding two charging platform at ~3.4V and ~3.1V, respectively. Apparently, Li^+ prefers to insert into FeF_3 step by step, as described in reaction (6) and (7), which coincides with the previous reports.[51-52]

Fe_2O_3 is responsible for differences between the S400/SP and S500/SP. On one hand, Fe_2O_3 , as a remarkable composition for S500/SP shown in Figure S2, has higher electronic

conductivity than FeF_3 [27], which decreases the value of R_{ct} (Figure 4d). On the other hand, Fe_2O_3 has no contribute to capacity because the discharge platform of Fe_2O_3 is not higher than 2V[53-56], resulting in decreasing of capacity in the voltage region from 2V to 4.5V , as shown in Figure 4(a-c). However, unlike Fe_2O_3 , FeF_2/C can deliver a capacity of $\sim 135 \text{ mAh g}^{-1}$ in above voltage region according to our previous study[34], resulting in the better rate performance of S400/SP than S500/SP. In addition, amorphous PEG cannot evaporate at 200 °C and it would hinder Li^+ transport in S200/SP. Thus, better rate capability of S400/SP than S200/SP can be attributed to the poor Li^+ transport in S200/SP.

3. Conclusion

In summary, the $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor with high crystallinity and flower-like morphology can be synthesized by liquid precipitation method, and the self-assembling mechanism has been verified. The active iron fluoride samples can be obtained by heat treatment of the $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor, and followed by high energy ball milling with SP successively. The subsequent electrochemical testing reflects two different reaction mechanisms, corresponding to as-obtained FeF_3 or $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ at different temperatures. Furthermore, the hydration water in iron fluoride is proven to play an important role in cycling stability of the composite electrode, because it can reduce the ionicity and improve the electronic conductivity, and the inner hexagonal tunnel in $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ can facilitate the insertion and extraction for Li^+ . The optimized $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ sample S300/SP achieves a noticeable initial discharge capacity of 187 mAh g^{-1} as well as excellent cycling and rate performances, which indicates the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ composite is a promising cathode material for high capacity rechargeable Li-ion batteries.

In general, moisture should be restrictly avoided in lithium ion batteries due to its high reactivity towards lithium metal and electrolyte. However, this study showed that moderate “crystal” water is beneficial to construct different tunneled structure of iron fluoride.

Furthermore, the strategy of introducing exogenetic species to adjust the internal tunnel is expected to be an efficient way to design and adjust the structure-function relationship of the desired electrode materials for advanced secondary batteries.

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Figure Captions

Scheme1. The sketch map of the preparation route of different iron fluoride samples.

Figure 1. (a) SEM image, (b) Magnified SEM image and (c) XRD patterns of the self-assembly $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor.

Figure 2. SEM images of the $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ after standing for 0h (a), 3h (b), 6h (c), 9h (d), 12h (e), 15h (f); Schematic illustration of growth mechanism for flower-like particles (g).

Figure 3. HRTEM images showing the atomic structures of the S300/SP (a, b) and S500/SP (c) particles. The insets are atomic modeling with yellow spheres for Fe and red for F.

Figure 4 . (a) Cycling profiles of different iron fluoride samples at 0.1C in the voltage of 2.0-4.5 V ($1\text{C}=237 \text{ mAh} \cdot \text{g}^{-1}$). (b) Corresponding capacity retentions profiles. (c) Rate capacity profiles of different iron fluoride samples. (d) Nyquist plots of different iron fluoride samples carried out at a frequency range of from 10^6 Hz to 10^{-1} Hz .

Figure 5. Normalized Fe K-edge XANES spectra of the SP300/Li cell during the first discharge (a) and charge (b) with the dash-dot lines presenting the normalized Fe K-edge XANES spectra of standard FeO and Fe_2O_3 , (c) 2D contour plots of normalized Fe K-edge XANES spectra of the cell during the first two cycles, and (d) the corresponding charge-discharge curve of the cell.

Figure 6. The chemical bond and the crystal structure of iron fluoride samples, (a) chemical banding between Fe and F, (b) and (c) are the schematic drawings of the structure of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ and FeF_3 , respectively.

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Ying Bai is currently an associate professor at Beijing Institute of Technology (BIT). Her research interests focus on electrochemical energy storage and conversion technology. Dr. Bai earned her bachelor degree from Applied Chemistry Division at Harbin Institute of Technology, China (HIT) in 1997. She completed her Ph.D. from School of Chemical Engineering & Materials Science at BIT in 2003. In 2013, she was awarded New Century Excellent Talents in University from the Chinese Ministry of Education. She hosted and is hosting the projects of the National Natural Science Foundation of China as a principal investigator. Dr. Bai has authored/co-authored more than 70 peer-reviewed articles and filed 25 Chinese patents.

Xingzhen Zhou received his B.S. degree from Beijing Jiaotong University in 2013, and M.S. degree in School of Material Science and Engineering at Beijing Institute of Technology in 2015. His research focused on the study of iron fluorides as cathode material for Li-ion batteries. He is currently working at the National Active Distribution Network Technology Research Center, Beijing Jiaotong University, where his main work is battery detection and diagnosis for electric drive vehicle.

Dr. Chun Zhan is a postdoctoral appointee in Chemical Sciences and Engineering Division at Argonne National Lab. Her research interests focus on electrochemical energy storage

technology, with the main focus on cathode materials of the lithium ion battery. Dr. Zhan earned her Ph.D. degree in Physical Chemistry in the Department of Chemistry of Tsinghua University in 2014.

Lu Ma is currently a PhD candidate in Department of Chemistry and Biochemistry at the Ohio State University. She is now a guest graduate student in Advanced Photo Source, Argonne National Lab under the supervision of Dr. Tianpin Wu. She received her B.S. in Materials Physics and Physical Science (with Honors) from University of Science and Technology of China (USTC) in 2011. Her current research is mainly focused on characterization of battery materials and Mo-S clusters.

Dr. Yifei Yuan obtained his Ph.D. majoring in Material Science and Engineering from Michigan Technological University and is currently a postdoctoral research associate working jointly at Argonne National Laboratory and University of Illinois at Chicago. His research interest is *in situ* electron microscopy of energy storage behaviors of rechargeable battery materials as well as *ex situ* battery electrochemistry.

Chuan Wu is a professor at Beijing Institute of Technology (BIT), where his interests are new energy materials, and secondary batteries based on multi-electron materials. He received his Ph.D. degree in Applied Chemistry from BIT in 2002, followed by a 2-year postdoctoral fellowship in Dalian Institute of Chemical Physics, Chinese Academy of Sciences. He is experienced in energy conversion and storage. Dr. Wu was awarded Beijing Outstanding Talents Cultivation Project in 2007, Beijing Nova Program Award in 2009, and New Century Excellent Talents in University in 2012.

Mizi Chen received her B.S. and M.S. degrees in 2011 and 2014 from Beijing Institute of Technology, where her research was focusing on environment friendly materials for Li-ion batteries. She is currently working at Xiamen Water Affairs Zhonghuan Sewage Treatment Co., Ltd.

Guanghai Chen is currently pursuing his Ph.D. under the supervision of Prof. Chuan Wu in School of Materials Science and Engineering at Beijing Institute of Technology, China. He

received a bachelor's degree of Applied Chemistry from Hubei University for Nationalities in 2014. His research mainly focuses on the study of metal fluorides for Li-ion and Na-ion batteries.

Qiao Ni received his B.S. degree in Applied Chemistry from Jiangxi Science and Technology Normal University in 2014. He is now pursuing his Ph.D. in School of Material Science & Engineering, Beijing Institute of Technology supervised by Prof. Chuan Wu. His research interests focus on electrode materials for rechargeable Na/Li-ion batteries.

Feng Wu is the director of the Green Energy Research Institute, and the vice president of the China Battery Industry Association. As the chief scientist, he has hosted the National Key Program for Basic Research of China (973 projects), Basic Research on New Rechargeable Batteries and Related Materials. He has published over 500 papers and has been awarded 45 patents. In 2012, he was awarded the IBA Research Award for outstanding research of battery material and systems for electric vehicles.

Reza Shahbazian-Yassar is an associate professor of Mechanical Engineering at the University of Illinois at Chicago (UIC). He received his PhD (with honor) in Materials Science from Washington State University in Pullman, WA, in Dec 2005. Prior to joining UIC, he was assistant professor and later promoted to associate professor rank at Michigan Technological University in Houghton, MI, during 2007-2015. Prof. Shahbazian-Yassar's research focuses on electrochemistry science at confined spaces and in-situ transmission electron microscopy. He was the recipient of 2014 Summer Faculty Fellow from ASEE and received the Young Leaders Awards from TMS in 2016. He has published more than 90 journal papers and 4 book chapters. He is the current President and former Materials Science Director for Midwest Microscopy Society, a member of Steering Committee for ASME NanoEngineering for Energy Committee, and the former chair of the Advanced Characterization, Testing, and Simulation (ACTS) Committee at The Materials Society (TMS). He is also a member of Editorial Board for *Metallurgical and Materials Transactions A* (MMTA).

Dr. Tianpin Wu is the principle beamline scientist working at beamline 9-BM of the Advanced Photon Source, Argonne National Laboratory. Her expertise is in energy storage and catalyst materials characterization by X-ray Absorption Spectroscopy. She received her undergraduate degree in Chemistry from the Univ. of Science and Technology of China, and her Ph.D. degree in Physical and Analytical Chemistry from the Univ. of Utah. Following two and half years of postdoctoral research in the Division of Chemical Sciences and Engineering at Argonne National Laboratory, she joined the X-ray Science Division as a physicist in 2012.

Dr. Jun Lu is a chemist at Argonne National Laboratory. His research interests focus on the electrochemical energy storage and conversion technology, with main focus on beyond Li-ion battery technology. Dr. Lu earned his bachelor degree in Chemistry Physics from University of Science and Technology of China (USTC) in 2000. He completed his Ph.D. from the Department of Metallurgical Engineering at University of Utah in 2009 with a major research on metal hydrides for reversible hydrogen storage application. He is the awardee of the first DOE-EERE postdoctoral fellow under Vehicles Technology Program from 2011-2013. Dr. Lu has authored/co-authored more than 180 peer-reviewed research articles and has filed over dozen patents and patent applications.

Dr. Khalil Amine is a Distinguished Fellow and the Manager of the Advanced Battery Technology programs at Argonne National Laboratory, where he is responsible for directing the research and development of advanced materials and battery systems for HEV, PHEV, EV, satellite, military and medical applications. Dr. Amine currently serves a member of the U.S. National Research Council on battery related technologies. Among his many awards, Dr. Khalil is a 2003 recipient of Scientific America's Top Worldwide Research 50 Research Award, a 2009 recipient of the US Federal Laboratory Award for Excellence in Technology Transfer, and is the five-time recipient of the R&D 100 Award, which is considered as the Oscar of technology and innovation. In addition, he was recently awarded the ECS battery technology award and the international battery association award. Dr. Amine holds or has

filed over 130 patents and patent applications and has over 280 publications. From 1998-2008, Dr. Amine was the most cited scientist in the world in the field of battery technology.

$\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ nano-flakes precursor with high crystalline degree and beautiful flower-like morphology is synthesized successfully by liquid precipitation method and the self-assembling mechanisms are investigated and discussed. Subsequently-prepared $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ and FeF_3/C nanocomposites are used as cathode materials for lithium ion batteries. Hydration water is proven to play an crucial role in the structure and electrochemical performances of the iron fluoride.